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Research Article

Adsorption of Amaranth Dye from Aqueous Solution Using Environmental Friendly Biosorbents-eggshell Powder

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Abstract

Background and Objective: Dyes and pigments have been used in many industries for coloration purpose but they pose hazards to environment and end users of water. Therefore, it is important to remove these pollutants from wastewater before their final disposal. This work aimed to investigate the removal of amaranth dye by cost effective, eco-friendly, highly efficient adsorbents such as egg shell powder and environmental friendly biosorbent. **Materials and Methods:** The adsorption of anionic amaranth dye by egg shell powder was carried out by varying different parameters which include contact time, pH, adsorbent dosage and temperature to study their potential in adsorption of adsorbent. **Results:** The results obtained that optimal adsorption of dye was noticed at pH 4 (98.32%), temperature 60°C (96.30%) with 6 g of egg shell powder (97.61%) and has saturation point at 300 ppm after which desorption of dye occurs. The adsorption process was analyzed by the Langmuir, Freundlich and Temkin isotherm models. The adsorption of amaranth was best represented by Freundlich model. **Conclusion:** Egg shell powder is eco friendly bio adsorbent and it can be used for amaranth dye removal.

Key words: Dye, adsorption, wastewater, eggshell, amaranth, absorption kinetics

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The earth acquires waste from various industries; those wastes have been classified degradable and non-degradable. Degradable wastes can be removed by various biological sources and non-degradable waste after a series of treatment then it can be disposed to the environment¹. After disposal the waste materials are degrading the soil properties and contaminating water bodies. For examples industries dye waste, large quantities of synthetic dyes are used by the textile and dying industries, these dyes are released into the environment in the form of effluents during synthesis and dying process by which public health and environment are threatened. It is difficult to treat dye wastewater because of the synthetic and complex structure of the dye. The aromatic rings in the molecular structure of the azo dye cause these effluents to be toxic and non-biodegradable². Removal of toxic effluent from wastewater occurs either by biological methods or physicochemical methods. The treatment methods used are oxidation reduction, reverse osmosis, coagulation, filtration, ion exchange, adsorption, electro dialysis etc. Because of high cost and disposal problems, these conventional methods have not been applied to large scale industries. Adsorption is superior to other techniques in terms of low-cost, flexibility, simplicity of design, ease of operation and insensitivity to toxic pollutants³. Amaranth dye is an anionic azo dye, which is widely used for colouring natural and synthetic fibres, paper, wood, leather, cosmetics, phenol-formaldehyde resins as well as in photography and as a food and beverage additive. Its name was taken from Amaranth grain, a plant distinguished by its red colour and edible protein-rich seeds. It usually comes as a disodium salt. Amaranth is extensively used in textile industries as a food dye and to color cosmetics but since 1976 it has been banned in the United States by the Food and Drug Administration as it is a suspected carcinogen⁴. High concentrations of amaranth dye can adversely affect human and animal health and cause tumors, allergic and respiratory problems as well as birth defects in human being⁵. The efficacy of adsorption process for the removal of dyes is well documented but this method is expensive and hence finding a low cost adsorbent is the need of the hour. Many low cost adsorbents have been reported like siliceous materials, coffee husk-based activated carbon, clay materials, zeolites, marine algae, chitosan to name a few. In the present study, eggshell powder is used as an adsorbent for the removal of dyes from aqueous solution. It contains more percentage of calcium carbonate and less amount of magnesium carbonate, calcium phosphate. Many reports suggested the use of egg shell powder as an adsorbent in the removal of methylene

blue, Rhodamine B, Eriochrome black T and Murexide dyes, Acid blue 92, Reactive Red 35 (RR 35) etc^{6,7}. The egg shell is an ubiquitous material that is available all around the world. Also the egg shell powder contains calcium carbonate, magnesium carbonate and calcium phosphate. The aim of this study was to remove the amaranth dye from aqueous solution by using chicken egg shell powder and to study the adsorption kinetics.

MATERIALS AND METHODS

Absorbent preparation: The chicken egg shell was collected from the food processing centre, Sathyabama Institute of Science and Technology, Chennai. Eggshell was washed thoroughly until remove the egg white with distilled water and dried at 100°C. Dried waste shell was crushed and converted to a fine powder of 85 micron size mesh particles. The egg shell contains various elements such as 94% calcium carbonate, 4% magnesium carbonate, 3% protein and 1% organic matter⁸.

Biomass characterization: The biosorbent materials were characterized by Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) before being used and after the adsorption process, to check possible changes resulting from the biosorption process.

Preparation of amaranth dye solutions: The dye solution were prepared at 1000 mg L⁻¹ by dissolving Amaranth dye (azo dye) in deionized water. Working standards were prepared from standard dye solution was analyzed using UV spectrophotometer.

Effect of initial dye concentration: Batch adsorption was conducted with series of initial dye concentrations ranging from 10-250 ppm. The absorbance was determined by UV spectrophotometer (Cary-Varian 300) at 520 nm and values were plotted for standard graph.

Adsorption studies: A stock solution of amaranth dye (1 g/100 mL) was prepared and diluted accordingly to the required initial concentrations (10-250 ppm). The adsorption studies were carried out at room temperature. Egg shell (1.0-7.0 g) were added in 100 mL of dye solution with desired concentration and stirred at 120 rpm for 168 h. The samples were centrifuges at 5000 rpm and the supernatant was analyzed using UV-Vis spectrophotometer. The experiments were conducted in triplicate.

Effect of pH and temperature: Amaranth dye solution prepared by addition of 1 N HCL and 1N H₂SO₄ with various range of pH 3-7 and treated with 6 g of egg shell powder and followed the adsorption were studied. Similarly, the amaranth solution prepared and kept at various temperatures (15, 40, 50, 60°C) and adsorption was studied⁹.

Effect of contact time: The contact time was varied in the range 0-168 h between the adsorbate and adsorbent to study the time-dependent behavior of the adsorption of amaranth into egg shell powder. The initial concentration of amaranth was kept at 50-350 ppm and the adsorbent dose was 6 g at temperature 60°C. The solution was centrifuged for 15 min for 5000 rpm and absorbance of supernatant was determined using UV spectrometer.

Adsorption kinetic models: Amaranth dye solution was prepared (pH 4) with various concentration (50-350 ppm) with 6 g of egg shell powder and kept at 60°C. Then adsorbed amount of dye and equilibrium concentration (C_e) was analyzed to determine the adsorption isotherms dye on egg shell powder by plotting a graph between extent of adsorption (log q) and equilibrium concentration⁹ log C_e.

Langmuir isotherm model: The Langmuir isotherm assumed that adsorption occurs on a homogeneous surface. The linear form of the Langmuir adsorption isotherm Eq. is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K \cdot Q_m} \quad (1)$$

where, C_e is the equilibrium concentration of adsorbate in the solution (mg L⁻¹), Q_e the amount of adsorbate adsorbed on the adsorbent at equilibrium (mg g⁻¹), Q_m the monolayer adsorption capacity (mg g⁻¹) and K is the Langmuir adsorption equilibrium constant (Lm g⁻¹), which is related to the energy of adsorption. The Langmuir constants, Q_m and K were determined from the intercept and the slope of the straight line obtained by plotting (C_e/Q_e versus C_e)⁹.

Freundlich absorption isotherm: Freundlich model suggested that adsorption process involves heterogeneous adsorption with different classes of adsorption sites. The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogeneous surface is given by:

$$\text{Log } Q_e = \text{Log } K_f + \frac{1}{n} \text{Log } C_e \quad (2)$$

where, Q_e is the quantity of solute adsorbed at equilibrium (mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at a equilibrium (mg L⁻¹). K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent respectively. The Freundlich isotherm constants are calculated from the plot of (log Q_e vs. log C_e)⁹.

Temkin adsorption isotherm: The Temkin model proposes into account the effects of the interaction of the adsorbate and the adsorbing species¹⁰. By ignoring the extremely low and large concentration values, the model assumes that the heat of adsorption (a function of temperature) of all of the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate-adsorbent interactions is given by:

$$q_e = \frac{RT}{b} \log (K_T C_e) \quad (3)$$

where, B = RT/b Temkin constant related to the heat of adsorption (kJ/mol) and K_T empirical Temkin constant related to the equilibrium binding constant related to the maximum binding energy (L mg⁻¹)⁹.

FTIR analysis: The FTIR was used to elucidate the functional groups present on the surface of the adsorbent that may be involved in the removal of amaranth dye from aqueous solutions. Adsorbent sample were brought into contact with amaranth dye solutions at a concentration of 300 ppm, at pH 4 for 168 h and 60°C to saturate the binding sites with the dye. The suspension was centrifuged for 10 min at 5000 rpm and the pellet was washed twice with distilled deionized water to remove the unbound dye. Then, after centrifuging the resulting suspension, the obtained dye-loaded biosorbent was oven-dried at 105°C in order to remove any water retained which could interfere with the observation of hydroxyl groups on the biosorbents surface. The characterization of egg shell powder was done by Fourier Transform Infrared Spectroscopy to elucidate the changes in functional groups. The sample was analyzed FTIR spectrophotometer using (Bruker Optic GmbH Tensor 27). The egg shell particles were mixed uniformly with Potassium bromide. The KBr discs were prepared by compressing the powders (egg shell powder and KBr) at pressure 5 t for 5 min in hydraulic press¹¹.

SEM analysis: Egg shell powder particles shape and size morphology was studied by field emission scanning electron

microscope. In a SEM set up, the egg shell powder particles coated to be conductive is scanned in a high vacuum chamber with a focused electron beam using (Supra 55 Carl Zeiss Germany) magnification range 35-10,000 resolution 200 A acceleration voltage 19 kV.

Statistical analysis: Mean \pm SD and regression analysis was done to analyze data.

RESULTS AND DISCUSSION

Industrial dye effluent which is a source of different dyes poses serious impact on the environment. Looking for methods to treat the dyes is a consistent process. In view of this, the present study involves the use of eggshell powder as adsorbent for removal of amaranth dye from the aqueous solution.

Time course of dye concentration: The time course of dye concentration was evaluated against the adsorbent dosage and time. In the present study (Table 1) the adsorption of amaranth dye on eggshell powder was experimented at different amaranth dye concentration (50-350 ppm). When 5 g of adsorbent was added to 50 ppm of dye, it was observed that the total dye removal was 100%. When the dye concentration was increased the adsorption was found to decrease stating that 5 g was not sufficient to bring about adsorption for higher concentrations of dye. Hence, adsorption of dye was done

using 7 g of adsorbent for 50-350 ppm. From this, it was observed that with increase in dye concentration the adsorption efficiency increases till it attained equilibrium due to large surface area and more active site for dye adsorption. This also may be due the driving force which overcomes the mass transfer resistance of the dye molecules between the aqueous and solid phase. At 300 ppm for 6 g of adsorbent, the percentage of dye removal was found to be 98.96% and after this there is decrease in adsorption capacity. There are many factors effecting the rate of adsorption including, dye structure, size or molecular weight, concentration and the charged groups¹². Similarly, Salman *et al.*¹³ reported that maximum concentration of Congo red was at 400 mg L⁻¹ which was absorbed by barnacle shell powder. The same results was also observed by Habeeb *et al.*¹⁴ reported that chicken eggshell can be used to remove the H₂S gas from the wastewater. Further he added that at 250 mg L⁻¹ have adsorption capacity was found to be maximum.

Effect of adsorbent dosage on dye removal: The effect of adsorbent dosage was investigated for dye adsorption by varying the adsorbent dosage from 2.5-7 g (Table 2). The dye removal efficiency increased with adsorbent dose due to increased sorbent surface area and number of adsorption sites for dye. From the result, it was came to know that 6 g of adsorbent is best for dye adsorption and the similar trend was observed by Gong *et al.*¹⁵. The porous nature of eggshell makes it an attractive material to be employed as an adsorbent.

Table 1: Time course of dye concentration

Dye Conc. (ppm)	Days									Dye removal (%)
	0	1	2	3	4	5	6	7		
50	47	37	21	12	5	0	0	0	0	100.00
100	101	89	70	58	20	3	0	0	0	100.00
150	140	140	128	100	75	55	20	3	3	97.86
200	196	175	142	110	78	56	20	3	3	98.47
250	248	210	170	138	106	58	20	3	3	98.79
300	288	250	200	154	120	85	35	3	3	98.96
350	346	290	230	188	150	100	48	13	13	96.24

Table 2: Effect of adsorbent dose on dye adsorption

Adsorbent dose (g)	Days										Dye removal (%)
	0	1	2	3	4	5	6	7	8	9	
2.5	290	248	216	46	48	44	42	41	39	10	96.55
3	298	245	45	44	40	41	40	40	39	8	97.32
3.5	297	246	42	39	39	36	35	33	31	10	96.63
4	298	249	47	46	43	43	41	39	36	12	95.97
4.5	297	250	49	46	44	40	39	37	35	9	96.97
5	298	247	39	20							93.29
6	297	244	35	13							95.62

It was estimated that each eggshell contains between 7000-17000 pores¹⁶. Also there are reports that heat treatment of eggshell powder at 150°C was found to increase the adsorption capacity¹⁷. Similarly Ahmadzadeh-Hakimi *et al.*¹⁸ reported that eggshell powder treated under 800°C followed by zinc and triethylamine solution brought about 98% removal of acid blue dye 92. Tsai *et al.*¹⁹ have reported that eggshell membrane is also efficient in removing heavy metals like nickel and silver due to the similarity between the properties of the egg shell powder and its membrane.

Effect of pH on dye removal: The effects of pH on amaranth adsorption using eggshell were investigated and the results are illustrated in Table 3. The pH is an important process factor in adsorption of dye from aqueous solution. Table 3 illustrated that adsorption of amaranth dye by eggshell decreased with increase in pH (3-7). The rate of adsorption at pH 4 was seen significantly higher than other pH. Beyond pH 4, there was no further increase in adsorption capacity. This was because at low pH, the eggshell is positively charged which will lead to significantly strong electrostatic attraction between the positively charged eggshell powder and the anionic dye molecules thus leading an increase in dye adsorption as well as the negative sites on the surface of eggshell. Thus, the eggshell with negatively charged sites will repel the anionic dye. As a result, it was interpreted that amaranth dye was best adsorbed by eggshell powder in acidic condition and quite difficult or almost unable to remove in alkaline condition. Similar observation was reported for removal of methylene blue dye using eggshell powder by Ngadi *et al.*²⁰.

Effect of temperature on dye removal: The effect of temperature was investigated for dye adsorption and the experimental results are mentioned in Table 4. The experimental result revealed that eggshell powder exhibit best adsorption affinity with the dye molecules at 60°C due to enlargement of pore size from where dye adsorbed and also adsorbent mass attributes to increased penetration of reactive dyes inside the adsorbent at higher temperature or creation of new active sites. The Pramanpol and Nuttakan²¹ reported that eggshell with membrane powder adsorbed maximum reactive dye concentration observed was at 35°C.

Effect of contact time on dye adsorption: The removal efficiency of amaranth dye with time was investigated for 300 ppm at 6 g of adsorbent dose (Table 5). A series of experiment were conducted to determine the equilibrium time for the adsorption. The adsorption process took in 168 h due to attractive forces developed between dye and adsorbed surface and further lead to no significant adsorption of dye the adsorbent as concentration driving force continuously decreases with time (t). Same results was observed by Ali *et al.*⁴ for the removal of amaranth dye from aqueous solution using pomegranate peel.

FT-IR analysis: FT-IR analysis of native adsorbent and dye loaded adsorbent is done to elucidate the functional groups responsible for the dye removal (Fig. 1). Interaction of dye with dye loaded adsorbent were compared with those of native adsorbent. FTIR analysis

Table 3: Effect of pH for dye removal

pH	Concentration (ppm)							Dye removal (%) $\frac{C_i - C_f}{C_i} \times 100$
	Days							
	0	1	2	3	4	5	6	
3	291	220	176	138	101	74	28	90.38
4	298	209	154	119	84	48	5	98.32
5	295	213	168	121	95	73	10	96.61
6	293	224	160	123	101	79	55	81.23
7	294	221	152	128	93	74	58	80.27

Table 4: Effect of temperature on dye adsorption

Temperature (°C)	Days							Dye removal (%) $\frac{C_i - C_f}{C_i} \times 100$
	Days							
	0	1	2	3	4	5	6	
15	298	222	199	153	110	78	52	82.55
30	299	231	201	177	122	86	45	84.94
45	299	235	211	182	137	91	40	86.62
60	298	212	185	146	92	65	11	96.30
75	299	220	179	150	110	80	45	84.94

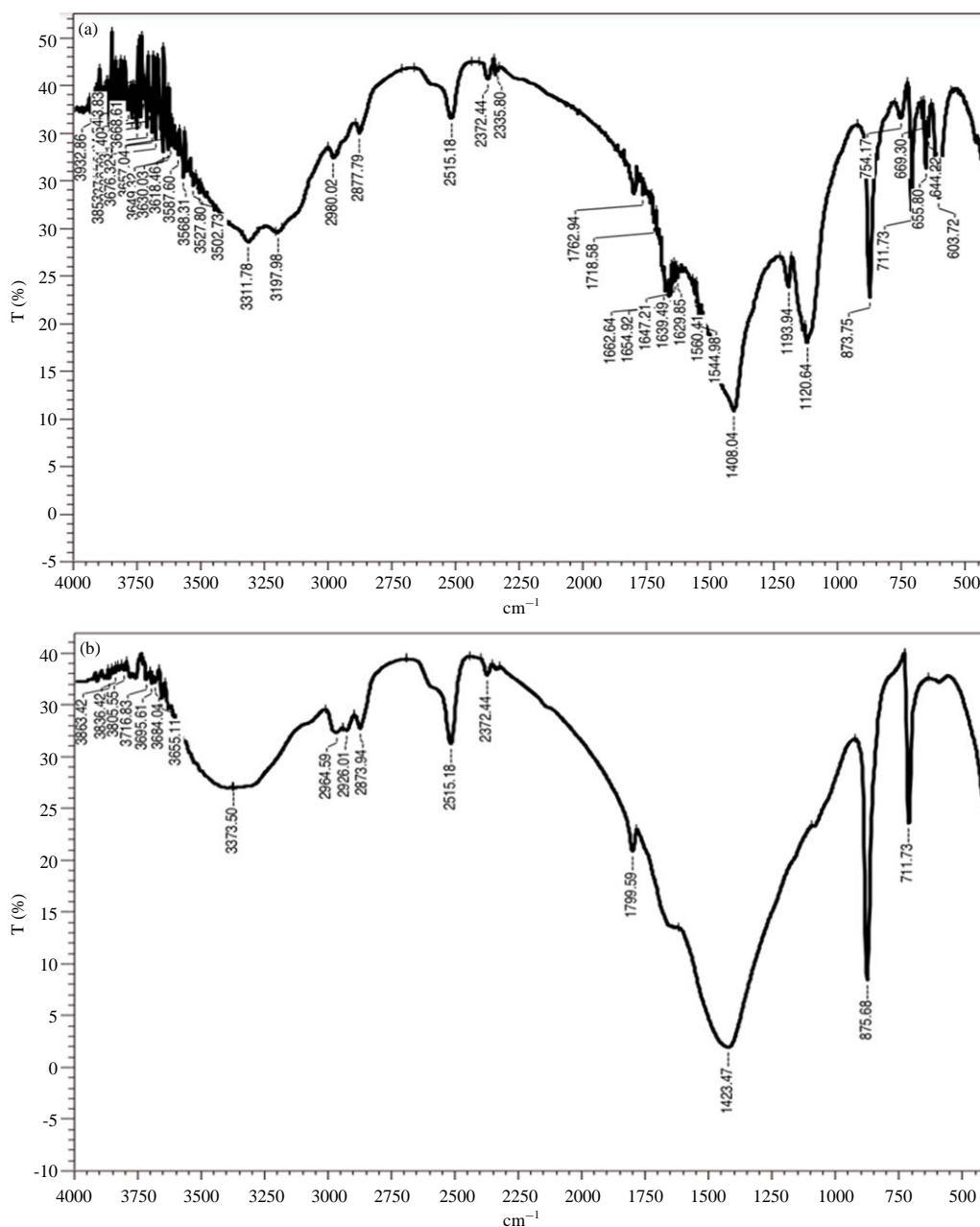


Fig. 1(a-b): FT-IR analysis (a) Before adsorption and (b) After adsorption

Table 5: Effect of contact time on dye removal

Contact time (h)	0th h	24 h	48 h	72 h	96 h	120 h	144 h	168 h
Dye removal (%)	0.4	16	32	44.8	57.6	76.8	92	98.88

of the native adsorbent showed peak at 3311.78 cm^{-1} for secondary amino (N-H) stretch. The peak at 2980.02 and 2877.79 cm^{-1} is due to C-H stretch vibration for methyl ($-\text{CH}_2$) and methylene ($>\text{CH}$) groups. The sharp peak at 2515.18 and 1408.04 cm^{-1} are for acid (OH) and phenol. Also, the sharp peak at 1120.64 and 873.75 cm^{-1} are due to the vibration of

organic sulfates (C-H stretch) and aromatic PO_4 . The spectra of native adsorbent revealed many adsorption peaks in the 800-600 cm^{-1} region, which may be due to alkyl halide (C-H stretch). Among these changes was the narrowing of the band at the 3800-2500 cm^{-1} region, which may be due to a reduction in number of hydrogen bonds caused by the

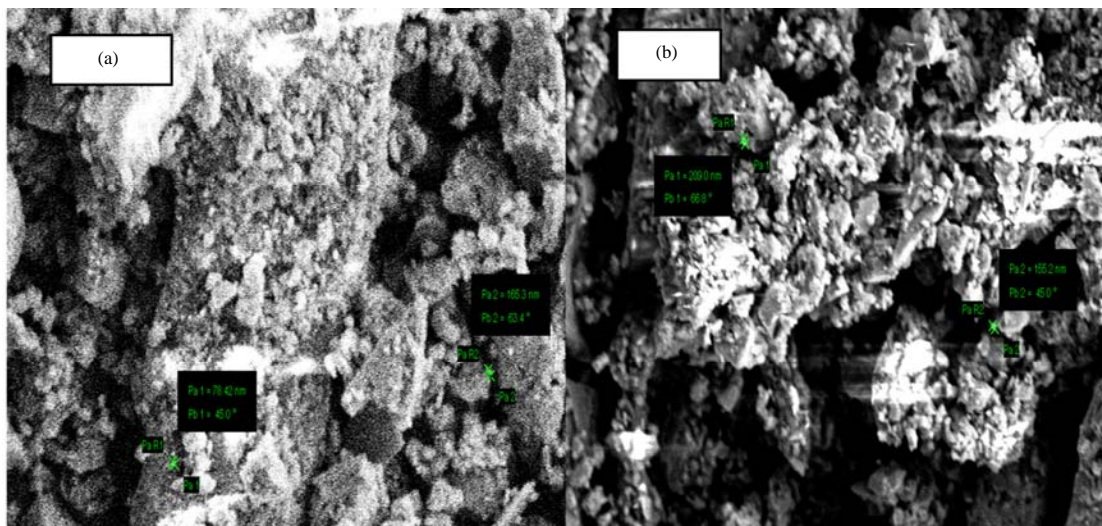


Fig. 2(a-b): SEM Analysis (a) Before adsorption (b) After adsorption

Table 6: Adsorption isotherm

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
Q_m	K_L	R^2	$1/n$	K_f	R^2	$B = RT/b$	K_T	R^2
2.032	0.0038	0.916	0.706	0.596	0.968	3.724	0.209	0.921

interaction of the dye with the -OH and -NH groups of adsorbent. In addition, the sharp peaks at 1799.59, 1423.47, 875.68 and 711.73 cm^{-1} may be for acid anhydride, carboxylate (carboxylic acid salt), peroxides(-C-O-O-C-) which helps in dye adsorption. From the results, the chemical interactions between adsorbent hydroxyl, carbonyl and amine group and the dye molecules were involved in dye adsorption (Fig. 1). The above results were observed by Guerrero-Coronilla *et al.*¹¹ for the biosorption of amaranth dye from aqueous solution using *Eichhornia crassipes*. Also this report supported that in acidic conditions is favour for amaranth dye and other sulfonic dyes binds to adsorbent surface due to electrostatic attraction by the amide groups of adsorbent.

SEM analysis: The SEM analysis illustrates the surface and characteristic morphology of the native adsorbent and the dye loaded adsorbent (Fig. 2). The images clearly show that the pores of the native adsorbent are of different shape and size which provide large surface area for dye adsorption. From the Fig. 2, it could be understand that porous surface texture increases the surface area as well as adsorption capacity. It indicated that the treatment of dye influences the orientation of the particle of adsorbent. Also, the SEM analysis was helpful to determine the surface morphology of an adsorbent. The

agglomerate, non-adhesive, porous and irregular surface structure of the adsorbent is distinctly observed in the SEM image.

Adsorption isotherm models: To optimize the design of sorption system to remove dye from aqueous solution, kinetic profiling of amaranth dye adsorption were carried out to determine the rate controlling mechanisms involved in adsorption process using Langmuir, Freundlich and Temkin isotherms.

Langmuir isotherm: The Langmuir constants, Q_m and K_L were determined to be 2.032 and 0.0038 from the intercept and the slope of the straight line obtained by plotting C_e/Q_e versus C_e . The correlation coefficient R^2 was found to be 0.916 and the adsorption was less favorable. The present study results (Table 6) were supported by Ali *et al.*⁴, who stated amaranth dye removal using pomegranate peel.

Freundlich isotherm: From the plot of $\text{Log } Q_e$ and $\text{Log } C_e$ showed in Table 6, the correlation coefficient R^2 was found to be 0.968. The value of n are less than 1, hence the process of adsorption is exothermic. The values of K_f and $1/n$ were calculated to be 0.59 and 0.706. From the values of $1/n$, it can be interpreted that the adsorption is more heterogeneous

in nature. The same results were observed by Abdullah *et al.*²² for the removal of p-nitrophenol using eggshell powder. Also the mean R^2 value obtained is 0.9403 by Borhade *et al.*⁶ using eggshell powder for the removal of Rhodamine B, Eriochrome black T and Murexide dyes from their aqueous solutions.

Temkin isotherm: As Table 6 illustrated the plot of $\log C_e$ and Q_e . From the results, the values were of correlation coefficient (R^2), K_T , B were calculated to be 0.921, 0.209 and 3.724, respectively and adsorption was found to favorable from the values of B (more the values of B, more favorable the isotherm is for physical adsorption process). The same trend was seen by Dada *et al.*²³ for the isotherm studies of equilibrium sorption of Zn+2 from phosphoric acid. Also the low cost rice husk used for the adsorption of amaranth dye by Chowdhury²⁴. From Table 6 obtained, the correlation coefficient values of Freundlich were higher than other correlations. This showed that Freundlich is the best fitting isotherm model for adsorption.

CONCLUSION

The present study is focused on the removal of amaranth dye from aqueous solution using eggshell powder as green and economic adsorbent. The maximum removal efficiency of adsorbent was found as 97.61% for 300 ppm at conditions of 6 g adsorbent dosage, 168 h contact time, pH 4 and 60°C temperature. The Freundlich isotherm was found to correlate better than the other isotherms with R^2 equals to 0.968. Therefore, the results conclude that eggshell powder is a potential adsorbent which is cost effective and environmental friendly for the removal of dye wastewater.

SIGNIFICANCE STATEMENT

The present study confirmed that eggshell is a good adsorbent for removing the dye. The eggshells are easily available, cost effective and can be converted into exploitable absorbent. The significance of this study is eggshell adsorbent has good porosity so it adsorbed maximum amount of dye concentration.

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